



A model for competitive electrolytic reactions involving gaseous species

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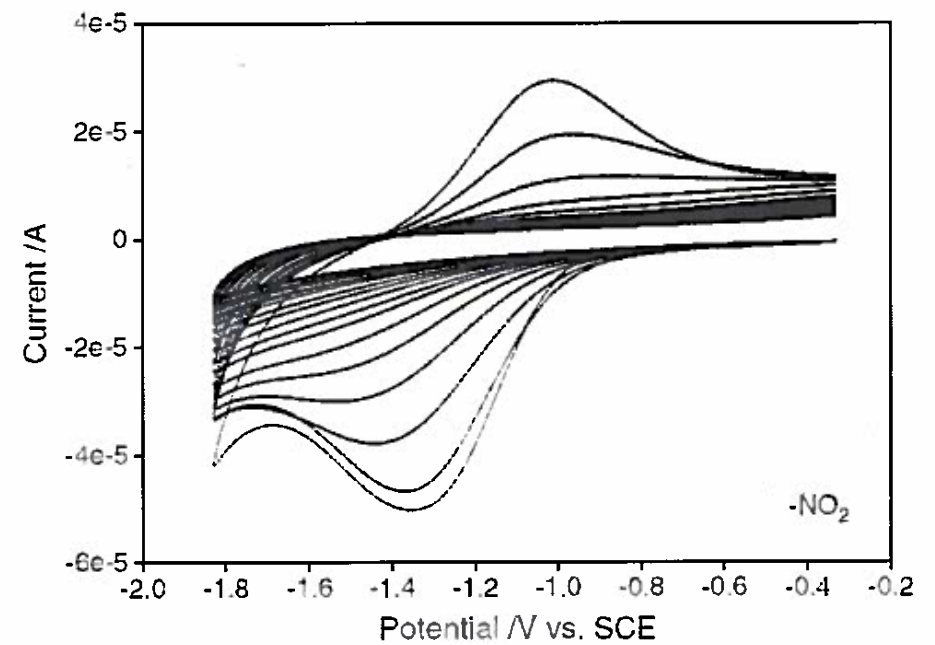
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Electrochemical Science and Technology



A two day conference





Electrochemical Science and Technology Conference 2012

We are glad to welcome all of the 34 participants to the Danish Electrochemical Society's two day conference on Electrochemical Science and Technology at Aarhus University October 11-12, 2012. This year program contains 16 oral and 7 poster presentations covering a broad range of aspects of electrochemistry. The main talk of the conference will be given by Prof. *Frédéric Kanoufi*, ESPIC Paris. One of the objectives of the conference is to generate a forum for exchange of knowledge and to strengthen the collaboration between industry and academia. We hope that you will have an interesting and informative conference.

We will like to thank Elplatek for sponsoring the student awards and Aarhus University for hosting the conference.

Torben Lund
(Chairman of Danish Electrochemical Society)

Mogens Hinge
(Chairman of the local organization committee)

Program Thursday 11/10

14:30-15:00 14:30-15:00 Arrival to Aarhus University, Fredrik Nielsensvej 4, Bygning 1421
8000 Aarhus C, in Meeting room 2.2.

15:00-16:00 General Assembly in the Danish Electrochemical Society

16:00-16:05 Welcome by Mogens Hinge, Department of Engineering, AU

Mini Symposium: Electrochemical Surface Modifications (Chair: Torben Lund)

16:05-16:50 *Kim Daasbjerg*, AU: Radical Ways of Functionalizing Surfaces

16:50-17:20 *Allan H. Holm*, Grundfos: Electrochemistry at Grundfos; joining of materials and water treatment

17:20-17:40 *Mie Lillethorup*, AU: Investigating Charge Transfer Processes in Ferrocene-containing Polymer Brushes

17:40-18:00 *Jesper Vinther*, AU: Redox-Active Layers Originating from Eletrogenerated Acid Facilitated Electrografting of Aryltriazenes

18:00-19:00 Check-in hotels, Tour at Chemistry, and Poster session in meeting room 2.2

19:00 - ? Conference dinner, Dept. of Chem. Cantina, Langelandsgade 140, 8000 Aarhus C.



Program Friday 12/10

- 9.00-9.05 Opening of the conference, Kim Daasbjerg
9.05-9.55 Invited Talk: *Frédéric Kanoufi*, ESPIC Paris Tech-CNRS: Inspecting the Local Reactivity of Surfaces from Their Electrochemical Triggering
9.55-10.25 *Palle S. Jensen et al*, DTU: Incorporation of Metallic Nanoparticles into Surface Molecular Assemblies for Enhancement of Long-Range Protein Interfacial Electron Transfer
10.25-10.40 Coffebreak
Oral presentations Session 1: Surface coatings (Chair: Mogens Hinge)
10.40-12.00 *Svava Davíðsdóttir et al*, DTU, Investigation of Photocatalytic Activity of Titanium Dioxide Deposited on Metallic Substrates by Plasma Technique
Rajnish Dhiman, SDU, SiCNanomaterials as Pt Catalyst Supports for Proton Exchange Membrane Fuel Cells
Torben Lund et al, RUC, The Role of N-Additives in Dye Sensitized Solar Cells
Lisbeth M. Ottosen et al, DTU, Electrokinetic Desalination of Portuguese Azulejo Tiles – Effect on Salt Crystals in the Interface between Biscuit and Glaze
12.00-13.00 Lunch
Oral presentations Session 2: Hydrogen production (Chair: Kim Daasbjerg)
13.00-14.20 *Juan Manuel Paz-Garcia et al*, A physiochemical and Numerical Model for Electrokinetics Transport
Cicilia Kjartansdóttir et al, DTU, Durable electrodes for Alkaline Water Electrolysis
Sune Egelund et al, Siemens, High-Efficiency, Low Cost Electrodes for Alkaline Electrolysis
Anders Thygesen, DTU, Upgrading of Straw Hydrolysate for Production of Hydrogen and Phenols in a Microbial Electrolysis Cell (MEC)
14.20-15.20 Poster Session and coffee
Oral presentations Session 3: E (Chair: Steen U. Pedersen)
15.20-16.00 *Shaung Ma Andersen et al*, SDU, Interaction Between Nafion Ionomer and Noble Metal Catalyst for PEMFC's
Anders Bentzen et al, AU, Experimental Evaluation of Electrokinetic Energy Conversion Efficiencies for Power Generation in Ion-Conductive Nano-Porous Membranes
16.00-16.15 Student awards
16.15-16.25 Closing remarks

Abstracts for Minisymposium

Thursday 11/10
16:00 – 18:00



REDOX GRAFTING OF DIAZOTATED ANTHRAQUINONE: NEW INSIGHTS

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The recently introduced term "redox grafting" refers to the electrochemically driven reactions of surface modification involving the redox active groups of the modifier. This process is brought about by an electron transfer from the surface of an electrode to the species confined to the surface which are capable not only of storing but also transmitting the charge to the outer part of the layer, thus making possible further reactions at the film-solution interface. If the newly added layer has redox stations (carbonyl, nitro groups) then the process would replicate itself upon a favorable potential, resulting in up to 1 μm film thicknesses.

A suitable system for fundamental studies of charge propagation events through conductive multilayers is the 1-anthraquinonyl (AQ) based films due to their reduced tendency for chemical degradation. In the present work the anthraquinone-1-diazonium tetrafluoroborate salt (AQD) was utilized to investigate the formation of AQ multilayers. Electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) technique was shown to be suitable for *in-situ* studying of the electrografting process. By the combining the cycling voltammograms with the frequency and dissipation changes from EQCM-D we have confirmed the proposed electron and solvated electrolyte transfer events accompanying electrografting.¹

References:

1. Chernyy, S.; Bousquet, A.; Torbensen, K.; Iruthayaraj, J.; Ceccato, M.; Pedersen, S. U.; Daasbjerg, K. *Langmuir* **2012**, *28* (25), 9573-9582



A MODEL FOR COMPETITIVE ELECTROLYTIC REACTIONS INVOLVING GASEOUS SPECIES

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A model is presented for the calculation of the faradic efficiency of chloride oxidation with respect to the water oxidation reactions in electrolytic processes of salted water. This model is designed to predict the ionic flux of incoming H^+ or outgoing Cl^- into an electrolyte as a consequence of these competitive electrolytic reactions. In the model, gases from the reactions, i.e. O_2 and Cl_2 , form mixed gas bubbles which are freely released from the surface of the electrode with a constant total pressure, P_T (atm), equal to the pressure of the surrounding atmosphere, as:

$$P_{\text{Cl}_2} + P_{\text{O}_2} = P_T$$

Using the Nernst equation, partial pressures of the different components are obtained as a function of the concentration of aqueous chloride and the pH value at the vicinities of the electrodes. In this context, electrochemical potentials for the half reactions are assumed to have the same value, being the partial pressures the determining factor.

$$E_{\text{Cl}_2} = E_{\text{O}_2}$$

Generally, Nernst equation predicts high faradic efficiency of water electrolytic reaction with respect to chloride. Bubble overpotential, a specific form of concentration overpotential due to the evolution of gas at either the anode or cathode, is included in the model to fit the evolution of chloride to the experimental results.



ASSESSMENT OF THE PERFORMANCE OF AN EDTA- ENHANCED ELECTROKINETIC REMEDIATION OF A CONTAMINATED SOIL

**María VILLÉN-GUZMÁN¹, César GÓMEZ-LAHOZ¹, Rafael A. GARCÍA-
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The use of BCR sequential extraction procedure at heavy metals contaminated soils for the prediction of the behaviour of some remediation techniques has proven to be an interesting tool. The success of these predictions are mainly observed for those techniques which are based on the mobilization of the toxic metals by acid, and the predictions can be correlated to the metals mobilized in the first fraction of the BCR, which uses acetic acid. Thus, when other mobilization agents are used, such as chelating agents, the use of batch extraction experiments can be a useful tool for the prediction of the behaviour of techniques such as EDTA-enhanced electrokinetic remediation (EKR). We explore this issue using the same contaminated soil of Linares with the main details given in other papers presented at this conference.

The electrokinetic experiments were performed in two small methacrylate columns (3.2 cm² cross section area and 2 cm length) that hold about 15.5 g of the water saturated soil each one. The two columns are electrically connected in series, thus assuring that the same electrical charge flows through both columns. All the experiments were performed at a constant current density of 2 mA cm⁻². The addition rate of the ligand is about half of the circulating rate of electrical charge through the soil. Thus, one mol of ligand is added to the cathode compartment for each 2 moles of electrical charge (e⁻) circulated. If it is assumed that di-acid ethylenediaminetetraacetate anions are the main carriers of the electrical charge at the catholyte-soil boundary surface this addition rate would prevent the depletion of EDTA anions in the catholyte.

Contrary to the expected results, Pb was not recovered at the anode, and about a 4% was recovered at the cathode. Furthermore, an electroosmotic flow of about 1.7 mL h⁻¹ was observed from the anode toward the cathode. Therefore, the Pb-EDTA complex ions are undergoing two transport phenomena in opposite directions: electromigration toward the anode and electroosmosis toward the cathode. This could explain the no removal of Pb from the soil. The confirmation of such hypothesis requires the mathematical simulation of the process which is the future work to be performed.

Acknowledgements: The authors acknowledge the financial support of the Spanish Government through the project ERHMES, CTM2010-16824.



ASSESSMENT OF THE PERFORMANCE OF HNO₃-ENHANCED ELECTROKINETIC REMEDIATION OF A CONTAMINATED SOIL

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When an electrical potential difference is applied between two electrodes inserted in the soil, the ions in the pore aqueous phase (including the heavy metal ions) are mobilized by electromigration towards the electrode of opposite charge where they are recovered, in a technique known as electrokinetic remediation (EKR). Frequently, water electrolysis reactions occur at the electrodes and generate an alkali and an acid front that migrate through the soil in opposite directions. This creates two possible problems: The basic front can cause metals precipitation and a low electrical-conductivity zone can arise in the region where the two fronts meet. To prevent these problems, an enhancement of the EKR technique consists in the addition of an acid to the cathode compartment.

This work studies the feasibility of a nitric acid-enhanced EKR of a soil from the ceased mining district of Linares (Spain). The soil samples for this study were collected at 10-30 cm depth, from a zone downstream from some slag heaps. The values obtained for the total concentrations of the most representative metals, in mg kg⁻¹, were Pb: 45200 ± 700, Mn: 2300 ± 200; Cu: 530 ± 16 and others in lower concentrations such as Zn, As, etc. A sequential extraction procedure is performed for each of these metals, indicating that their mobility is quite different, with more than 80% of the Pb soluble at a pH value about 2.4, whereas only about 50% of the Cu is solubilized at that pH value.

The very low hydraulic conductivity of this soil (below 10⁻¹⁰ m s⁻¹) makes EKR the only technique to be considered among the in situ ones. The electrokinetic experiments were performed in two small methacrylate columns (3.2 cm² cross section area and 2 cm length) that hold about 15.5 g of the water saturated soil each one. The two columns are electrically connected in series, thus assuring that the same electrical charge flows through both columns. All the experiments were performed at a constant current density of 2 mA cm⁻². Nitric acid solution is adequately added to the cathode compartments in order to hold the pH of the catholyte at a constant value. Around a 27% of the Pb in the soil was recovered at the cathode whereas the concentration of Pb in the half of the soil closer to the anode was reduced below 10% of the initial one.

Acknowledgements: The authors acknowledge the financial support of the Spanish Government through the project ERHMES, CTM2010-16824.



ASSESSMENT OF THE PERFORMANCE OF ACETIC ACID- ENHANCED ELECTROKINETIC REMEDIATION OF A CONTAMINATED SOIL

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When studying the remediation of soils contaminated by heavy metals the BCR fractionation has proven a very useful tool for the prediction of the performance of some techniques. On another paper presented at this conference we presented the results obtained for the remediation of a soil from the mining district of Linares (Spain) contaminated by heavy metals, mainly by Pb using the electrokinetic remediation (EKR) enhanced by the addition of nitric acid at the cathode compartment. In this case we use acetic acid instead.

The BCR results indicate that more than 80% of the Pb present in the soil is recovered in the first step of the fractionation analysis which uses acetic acid. Therefore we decided that EKR should give a good performance when enhanced by acetic instead of nitric acid.

The experimental setup and procedure is the same described in the other paper: two methacrylate columns electrically connected in series that hold 15.5 g of water saturated soil each, and which are crossed by a constant current with a density of 2 mA cm^{-2} . In this case, an acetic acid solution is adequately added to the cathode compartments in order to hold the pH of the catholyte at a constant value automatically controlled.

The recovery of Pb at the cathode is similar to that obtained with the strong acid enhancement (around a 30% of the Pb). Also the concentration profiles of Pb in the soil column are similar for the two types of enhancement. Nevertheless, the acid consumption rates at the cathodes are extraordinarily different. The protons addition rate for the acetic acid is more than four fold higher than that needed with the nitric acid, and than the rate of charge circulating through the soil. On the other hand, the time required for the achievement of a similar efficiency in the clean-up is 2.5 fold higher for the nitric acid than for the acetic.

The explanation of such differences requires the mathematical simulation of the process, which is the next step in the research work.

Acknowledgements: The authors acknowledge the financial support of the Spanish Government through the project ERMES, CTM2010-16824.

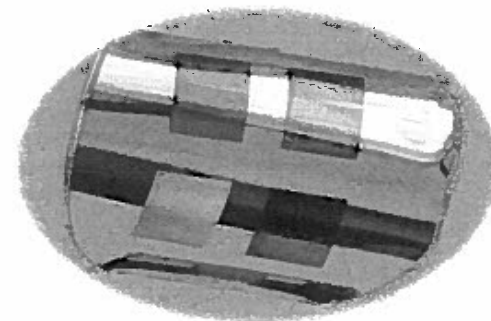


Electrochemical planarization of surfaces for micro- and nano- structuring

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By micro- and nanostructuring a surface it is possible to obtain self-cleaning properties, structural colors, light absorption, hydrophobicity, anti-stiction, increased friction or surface joining properties. The vision of the Danish High Technology platform "NanoPlast" is to develop and implement a technology that enables the use of nanostructured surfaces on injection moulded plastic components. The aim is to use nanotechnology in the production of plastic parts, where nanostructures are transferred from the surface of the injection moulding tool to the surface of the moulded plastic parts. This will enable new creative surface functionalities such as self-cleaning surfaces and structural colours in cheap plastic parts. The technology developed in the NanoPlast platform will enable nanostructures on free form moulded products. Today, mass production of nanostructured injection moulded surfaces can only be done when manufacturing planar items such as CDs and DVDs. In order to produce well defined micro- and nanostructures on the injection moulding tool, critical requirements are made to the surface roughness. As high precision polishing of the complex 3D surfaces of the injection moulding tool are extremely costly and time consuming, electrochemical processes have been sought for planarization of the surface. In this presentation, pulsed and DC deposition of Cu, Ni/Co alloy is attempted reduce surface roughness, and effect of pH and [Co] is investigated.





Electrokinetic desalination of Portuguese Azulejo tiles – Effect on salt crystals in the interface between biscuit and glaze.

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Ceramic tiles are an important part of Portuguese cultural heritage and are worldwide appreciated. Azulejo tiles decorate inner and outer walls of churches, gardens, private houses, railway stations and a series of other buildings. Many azulejo tile panels are damaged due to salt accumulation. Salts can crystallize on the surface or under the glaze, leading to severe damage as glaze lifting, fractures, scaling and granular disintegration.

Conservation actions today follow one of two approaches: either the tiles are removed from their support for ex-situ treatment (immersion in distilled water) before they are placed in the original place again or in-situ treatment of the azulejo panels by poulticing. Although poulticing is a well established technique, the results are still variable and unpredictable. Thus there is a need for a new in-situ technique which is gentle to the fragile azulejos.

Removal of salts from azulejos using an external DC field (electrokinetics) might be a potential method during conservation actions. The electrokinetic method has already experimentally been shown efficient for salt removal from natural stones, single bricks and from brick wall sections. Previously, few experiments have been made on electrokinetic desalination of single tiles, as well. These first experiments showed successful desalination when looking at average salt concentrations in the biscuit, however, it is the salt concentration in the interface between biscuit and glaze, which is the most important to decrease, as salt crystallization here causes disintegration of the glaze. The present study is focussed on this interface during electrokinetic desalination. Laboratory experiments are made with Portuguese XVIII century tiles which were removed from the panels due to salt decay. Before and after electrokinetic treatment the salt concentrations in the interface are evaluated using SEM-EDX.



A PHYSICOCHEMICAL AND NUMERICAL MODEL FOR ELECTROKINETIC TRANSPORT

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A physicochemical model is proposed for the mathematical description of electrochemically-induced transport processes, such as those taking place during electrokinetic treatments.

The model is based on the solution of the transient Nernst-Planck-Poisson system of partial differential equations. It includes the transport of water through the porous media due to capillary forces and electroosmosis, and the monitoring of the degree of saturation, the pH value and the porosity. Additionally, a comprehensive set of chemical and electrochemical reactions is included involving solid, gaseous and aqueous species and water in both the electrolyte and the solid structure.

A numerical model has been built for the mathematical solution of the proposed physicochemical model. This numerical model is based on a finite elements method for the integration of the transient system of partial differential equations, coupled with a Newton-Raphson method for computing chemical equilibrium. Electrochemical reactions are implicitly included in the finite elements method as part of the numerical procedure for the solution of the nonlinear system of equations.

The physicochemical and numerical model is described in a generalized manner. Therefore, it can be used to simulate a wide range of electrokinetic treatments in different inhomogeneous matrices, such as electro-desalination of construction materials and sculptures, electrokinetic remediation of contaminated soil or electrokinetic injection of matter into porous systems.